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Performance of sulfonated polystyrene–ethylene–butylene–polystyrene membrane in microbial fuel cell for bioelectricity production

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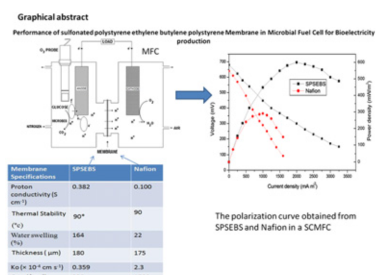
HIGHLIGHTS

- ► We demonstrate the use of SPSEBS membrane as alternate for the Nafion® 117.
- ► Enhanced power production observed in SPSEBS.
- ► Low oxygen diffusion property, resulted in high columbic efficiency.
- ► SPSEBS could be used by the MFC to overcome the drawbacks of Nafion® 117.

GRAPHICAL ABSTRACT



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ABSTRACT

Proton exchange membranes (PEMs) are an essential component for studying microbial fuel cells (MFCs), in spite of certain limitations and high operational cost. Present study reports the performance of a sulfonated polystyrene–ethylene–butylene–polystyrene (SPSEBS) membrane for application in MFCs. SPSEBS produces 106.9% higher power density and low internal resistance than Nafion 117® in a single chamber MFC (SCMFC). The oxygen mass transfer coefficient (K_O) is one order lesser in SPSEBS than in Nafion 117 thereby reducing substrate loss while increasing coulombic efficiency (CE). SPSEBS maintains a low pH gradient between the anode and cathode resulting in high performance. The change in the solution conductivities for Nafion is also much greater than that of SPSEBS. The results of this study indicate that SPSEBS could be a suitable PEM for improving the efficiency of MFCs.

1. Introduction

MFCs use bacteria to generate electric power by the oxidation of organic matter [1–5]. Bacteria have been reported to produce electricity directly by oxidizing domestic wastewater, ocean sediments, animal wastes and anaerobic sewage sludge [6,7]. In the anode chamber, microbes oxidize the substrate to produce electrons which are then transferred to the anode either by an exogenous electron carrier or a mediator (such as potassium ferricyanide, thionine, neutral red, methylene blue), or directly from the bacterial respiratory enzyme to the electrode in mediatorless MFCs. The anodic and cathodic chambers are separated by a proton conducting material, and externally by a wire that completes the circuit. In the cathode chamber, electrons that pass along the circuit combine with protons and oxygen to form water [8].

The important goals towards improving the performance of MFC are (i) to increase the recovery of electrons (CE) from the substrate and (ii) to reduce the material costs. Though membrane-free MFCs are promising in this regard, there are two major challenges associated with it. The first problem is that its CE is much lower when compared with MFC containing a membrane in a mixed culture. This is attributed to the loss of substrate due to the presence of

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oxygen that is diffused through the cathode. The second problem is associated with the distance between the anode and cathode in a membrane-free MFC which is limited to a certain range (about 1–2 cm) due to the potential negative effect of oxygen on the activity of the anaerobic bacteria on the anode along with the associated risk of short circuit. In addition, certain MFC designs like the flat plate MFC (FPMFC) need the use of membrane as their core component which makes it an unavoidable component [9–13]. Hence in this study, to overcome the above mentioned problems, MFC with a PEM was designed.

Nafion 117 membrane is one of the commonly used PEMs in MFCs, despite the existence of a number of problems associated with it such as high cost ($1500 m^{-2}) [14], oxygen leakage from cathode to anode, substrate loss, cation transport and accumulation rather than protons. Among these, oxygen leakage into the anode chamber can either lower the energy recovery due to the substrate loss from aerobic respiration by facultative bacteria, or inhibit the growth of obligate anaerobes [10,13–16]. The crossover of organic compounds (substrates and metabolites) from the anode compartment of an MFC to the cathode may considerably decrease the electrode performance due to the formation of mixed potentials and the flow of internal currents [17].

Several options towards finding alternatives like nanoporous polymer filters (nylon, cellulose, or polycarbonate) have been used effectively for Nafion as described earlier [18,19]. Though these are cost effective alternatives for Nafion, their drawback would favour oxygen transport. The majority of electrogenic bacteria have been observed to produce high power densities in anaerobic conditions. While the nanoporous membranes do not possess proton selectivity, the conventional PEMs have sulfonated groups which specifically facilitate transfer of protons to cathode.

One of the alternatives for Nafion 117 is sulfonated form of polystyrene–ethylene–butylene–polystyrene tri-block polymer. Polystyrene–ethylene–butylene–polystyrene (PSEBS) is a thermoplastic elastomer that consists of styrene blocks (thermoplastic phase) dispersed in ethylene–butylene matrix (elastomeric phase). It therefore, has excellent mechanical, chemical, and thermal stability. The sulfonated form of PSEBS, i.e., SPSEBS serves as a low cost polymer with good thermal and mechanical properties. The ionomer is based on a hydrocarbon network with an aromatic non-fluorinated backbone [20–22].

Present study reports the performance of an indigenous SPSEBS and the commercially available Nafion in SCMFC configuration. The pH gradient, change in conductivity and oxygen crossover of both membranes were identified in two-chamber MFC.

2. Materials and methods

2.1. Culture and medium

Bacteria from wastewater were used to inoculate the MFCs, since they are known to be suitable biocatalysts for electricity production [23]. MFCs were inoculated with the solution from an anode chamber of a one year operated MFC reactor which was originally inoculated with the domestic wastewater that was collected from Anna University sewage treatment plant (Chennai, India). The anode chamber was filled with wastewater inoculums containing the nutrient solution (1 g L^{-1} glucose, 0.1 g L^{-1} yeast, 0.5 g L^{-1} NaCl, 0.28 g L^{-1} NH_4Cl, 0.1 g L^{-1}, 0.68 g L^{-1} KH_2PO_4, 0.87 g L^{-1} K_2HPO_4), having a pH of 7 [24].

2.2. Electrolyte

Synthesis and characterization of PEM i.e., SPSEBS have been described in earlier reports [20–22]. The synthesized PEM showed good thermal stability, adequate ion exchange capacity (IEC) and excellent proton conductivity (Table 1). The tensile strength of SPSEBS membrane measured using UTM (Universal Testing Machine) was 3.05 MPa [21,22].

2.3. MFC construction and operation

The fabricated single chamber MFCs consisted of an acrylic cylindrical chambers 4 cm long by 3 cm in diameter (empty bed volume of 28 mL) separated by a (SPSEBS or Nafion 117) proton exchange membrane [14]. The anode electrode used was 30 wt.% wet proof carbon cloth [25]. The cathode was prepared using a carbon cloth having 0.5 mg cm^{-2} platinum coating as a catalyst. The experiment was carried out with a membrane electrode assembly (MEA) prepared by sandwiching the proton conducting membrane between the anode and cathode electrodes and then hot pressed at 70 °C, under 1 ton pressure for 2 min. The MEA was then assembled into the cylindrical SCMFC with the cathode-side of the MEA facing the air. Copper wire was used to connect the circuit with an external load. The experiment was conducted in fed batch mode at room temperature. All tests were done in triplicates and the average values were calculated.

The two-chamber MFCs (H-type) were designed by connecting two glass chambers (Schott Duran, graduated 250 mL bottle) as described earlier [8]. The SPSEBS membrane was indigenously prepared and used as a substitute for Nafion 117 in another two-chamber MFC of similar dimensions. The anode chamber containing the wastewater inoculated nutrient medium (250 mL, pH 7) was stirred continuously using a magnetic bar. The cathode chamber was filled with 50 mM PBS (pH 7) and was continuously sparged with air, which supplied oxygen. Two-chamber MFCs were used to study the effects of membrane permeability, solution conductivity and pH using oxygen probe, conductivity meter and pH meter respectively.

2.4. Analytical measurements and calculations

Cell voltage was recorded using a digital multimeter (model 702, Metravi, India). The circuit was completed with a fixed load of 1000 Ω; except when different resistors (100 Ω to 1 MΩ) were used to determine the power generation as a function of load. Current density was calculated as $I = V/RA$, where V (mV) is the voltage, I (mA) is the current density in electrochemical tests, R (Ω) is the external resistance, and A (cm^2) is the projected surface area of the electrode under study [13]. Internal resistance, R_{int}, of the reactors with different membranes was measured by electrochemical impedance spectroscopy (EIS) using a potentiostat (BioLogic VSP, France) with the anode as the working electrode and the cathode as

Table 1
Comparison membrane properties and cost.

Membrane specifications	SPSEBS	Nafion®
Polymer structure	Polystyrene-block–poly-(ethylene-ran-butylene)–block polystyrene	Co-polymer of tetrafluoroethylene (Teflon®) and perfluoro-3, 6-dioxa-4-methyl-7-octene-sulfonic acid
Proton conductivity (S cm^{-1})	0.382	0.100
Thermal stability (°C)	90[a]	90
Water swelling %	164%	22%
Thickness (μm)	180	175
K_O (×10^{-4} cm s^{-1})	0.359	2.3
Cost ($ m^{-2})	250	1500

[a] First weight loss from the TGA curve.

the counter and reference electrode. Impedance measurements were conducted at the open circuit voltage (OCV) over a frequency range of 10 kHz–0.1 Hz with sinusoidal perturbation of 10 mV amplitude. The ohmic internal resistances of reactors were determined using Nyquist plots as previously described [26]. The CE was calculated using the following equation:

$$CE = C_p/C_T \times 100\% \quad (1)$$

where C_p is the total Coulombs calculated by integrating the current over time. C_T is the theoretical amount of Coulombs that can be produced from glucose and is calculated as:

$$C_T = \frac{FbSv}{M} \quad (2)$$

where F is Faraday's constant (96,485 C mol^{-1} of electrons), b is the number of mol of electrons produced per mol of substrate (glucose) ($b = 24$ electrons per mole of glucose), S (g L^{-1}) the substrate (glucose) concentration, v the liquid volume (mL) and M the molecular weight of the substrate (glucose) ($M = 180$ g mol^{-1}) [9,13,14].

2.5. Oxygen transfer coefficients

The analysis of oxygen transfer coefficient for both Nafion 117 and SPSEBS membrane were performed under the same experimental conditions in a two-chamber MFC. Oxygen mass transfer coefficients were monitored using a portable dissolved O_2 probe (Extech 407510A, Taiwan) in the uninoculated and inoculated MFC reactors. The dissolved oxygen probe was attached to the lid of the anode chamber, and the analyte was sparged with nitrogen gas to remove dissolved O_2. Teflon tape was used to seal all the connections to prevent introduction of air into the chamber. The cathode chamber was continuously aerated to maintain saturated dissolved O_2 conditions. The mass transfer coefficient of oxygen (K_O) in the membrane was determined by measuring the dissolved O_2 concentration over time and using the following mass balances.

$$K_O = -V/At \ln[(C_O - C)/C_O] \quad (3)$$

where V is the liquid volume in the anode chamber, A is the membrane cross-sectional area, C_O is the saturated oxygen concentration in the cathode chamber, and C is the dissolved O_2 concentration in the anode chamber at time t. The diffusion coefficient (D_O, $cm^2\ s^{-1}$) was calculated as [10,14].

$$D_O = K_O L_t \quad (4)$$

where L_t denotes the membrane thickness (175 μm for Nafion 117 as reported by the manufacturer and 180 μm for the lab fabricated SPSEBS membrane).

3. Results and discussion

3.1. Performance evaluation of SPSEBS and Nafion membranes in an SCMFC

SCMFC with SPSEBS and Nafion 117 produced distinct variations in power density output (Fig. 1) when fed with successive batches of nutrient solution with glucose as substrate. The system start up was slow and the power density output rose after each batch feed, reaching a peak before declining due to consumption of the fuel. The peak power density increased from a value of 80 mW m^{-2} and 50 mW m^{-2} with the first batch of fuel for SPSEBS and Nafion 117 respectively, until a value of 590 mW m^{-2} and 280 mW m^{-2} were reached in the third batch. Beyond 300 h (i.e., third batch) no further increase in the output power density was observed which suggested that the anode biofilm was enriched with electrochemically-active bacteria thus rendering it stable. Subsequently the polarization curves were obtained using various resistances (1 MΩ–100 Ω) at 20 min interval period which was required for stabilization of the voltage. The SPSEBS membrane as the electrolyte produced a maximum power of 600 ± 14 mW m^{-2}, while Nafion produced only 290 ± 7 mW m^{-2} (Fig. 2), similar to the results obtained for Nafion as previously described [13]. Thus the SPSEBS membrane showed about 106.9% higher power density than Nafion although the electromotive forces were more or less same with values of 0.680 ± 0.03 V and 0.640 ± 0.04 V for SPSEBS and Nafion membranes, respectively. The Nyquist plots were used to obtain the internal resistance of Nafion that showed 125 Ω and only 70 Ω for SPSEBS (Supplementary data 1). The maximum coulombic efficiency produced was 85 ± 7% for SPSEBS and 51 ± 5% for Nafion. The SCMFC results showed conclusively that there was

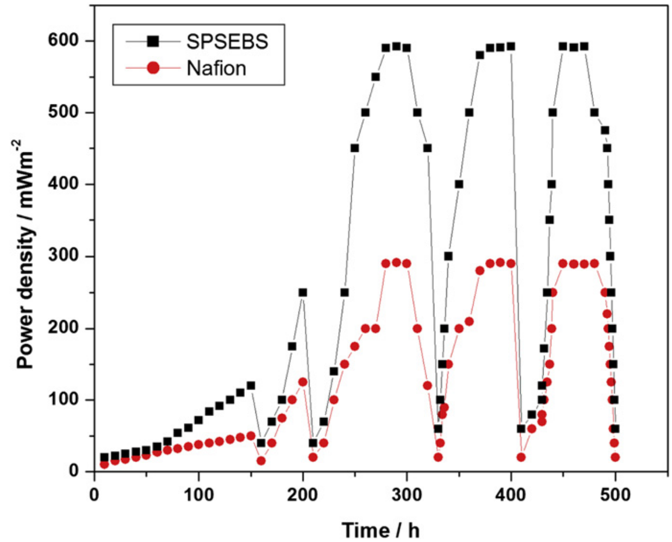

Fig. 1. Power generation verses time in a SMFC with SPSEBS and Nafion.

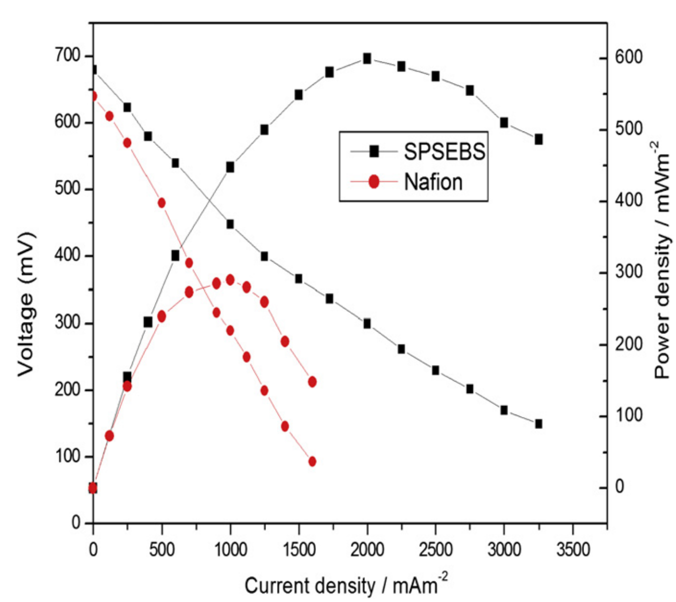

Fig. 2. The polarization curve obtained from SPSEBS and Nafion in a SCMFC.

a significant improvement in a performance of the MFC when SPSEBS membrane was used as a PEM.

3.2. Oxygen permeation through membranes

The dissolved oxygen concentration of the Nafion 117 based anode chamber increased from 0.18 to 1.4 mmol L^{-1} within 600 min due to oxygen transfer across the Nafion 117 membrane (Fig. 3). In contrast, when SPSEBS membrane was used as the PEM, the dissolved oxygen concentration of the anode chamber increased from 0.2 to 0.4 mmol L^{-1} only in 600 min. The oxygen mass transfer coefficient (K_O) and the oxygen diffusion coefficient (D_O) for Nafion 117 were estimated to be $K_O = 2.3 \times 10^{-4}$ cm s^{-1} and $D_O = 4.02 \times 10^{-8}$ cm^2 s^{-1}, respectively. The MFC with SPSEBS showed $K_O = 3.59 \times 10^{-5}$ cm s^{-1} and $D_O = 6.65 \times 10^{-9}$ cm^2 s^{-1}. This was one order lesser in magnitude than that of Nafion 117 and was the factor that facilitated the maximum power generation observed in SPSEBS. Chae et al reported a high K_O value (2.80×10^{-4} cm s^{-1}) for Nafion which was attributed to the high substrate loss resulting in low power generation due to oxygen permeation [11]. It is a well-known fact that electrochemically-active bacteria are facultative anaerobes that will switch from anaerobic to aerobic respiration in the presence of oxygen. It is however, noted that the aerobic respiration, resulting from the diffusion of oxygen through the membrane, generated less electrons when compared with anaerobic respiration [11,14,27]. Hence the higher power generation witnessed with SPSEBS is attributed to its low oxygen permeation.

3.3. Effect of membranes on solution pH in MFCs

Additional tests were conducted to study the effect of membranes on pH of the solutions using two-chamber MFCs with an initial pH of 7 for both anolyte and catholyte and pH changes were monitored. During a batch cycle, the pH decreased in the anode chamber due to substrate oxidation and proton production, while the pH increased in the cathode chamber due to proton reduction, consistent with previous reports [11,13]. In order to obtain a consistent current, for each electron that is produced, an equivalent proton must be transported to the cathode through the electrolyte [11,13,28]. While the pH of the anode and cathode solutions with Nafion was 4.4 and 10.3 respectively, it was 6.4 and 7.6 respectively for the SPSEBS. The pH drop in the anode chamber using the Nafion membrane was observed to be substantially higher (pH 4.4) than in tests with the SPSEBS (pH 6.4) due to its poor transfer of protons from anode to cathode. Protons produced from substrate oxidation were therefore not efficiently transported to the cathode chamber and accumulated in the case of anode chamber having the Nafion membrane. The properties of the SPSEBS membrane were superior to that of Nafion due to its high proton conductivity and water swelling (Table 1), which facilitate the proton transport efficiently from anode to the cathode chamber. The pH gradient across the SPSEBS was only 1.2 compared to 5.9 for Nafion due to its higher transfer of protons from anode to cathode. One of the reasons attributed for the improved performance of the membrane is the small pH gradients [26,29]. In addition, the change in the solution conductivities for Nafion was much larger than that of the SPSEBS. The solution conductivities changed from 8.7 mS cm^{-1} (anode) and 7.5 mS cm^{-1} (cathode) to 8.2 and 7.9 mS cm^{-1} respectively on using SPSEBS. With Nafion, the anode solution conductivity decreased to 5.9 mS cm^{-1} and the cathode conductivity increased to 10.1 mS cm^{-1}. The pH increase in cathode decreased the performance of Nafion in the MFC. The increase in solution conductivity at the cathode is attributed to the pH increase which affected the performance of Nafion compared to the SPSEBS.

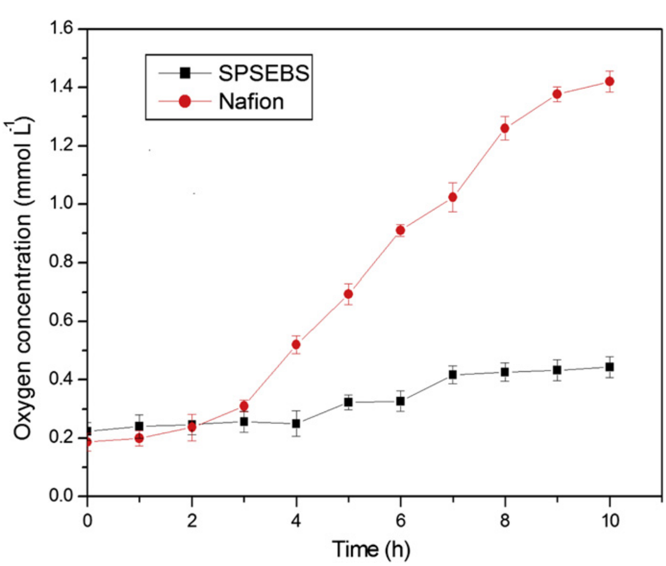

Fig. 3. Oxygen diffusion from cathode through Nafion and SPSEBS membranes in an uninoculated MFC (Nafion $K_O = 2.3 \times 10^{-4}$ cm s^{-1}, $D_O = 4.02 \times 10^{-8}$ cm^2 s^{-1}, SPSEBS $K_O = 3.59 \times 10^{-5}$ cm s^{-1} and $D_O = 6.65 \times 10^{-9}$ cm^2 s^{-1}).

4. Conclusion

This study demonstrates that the SPSEBS membrane has a great potential as PEM for MFC applications. SPSEBS shows 106.9% higher power density than Nafion. The internal resistance of SPSEBS produce only 70 Ω compared to 125 Ω for Nafion and also the oxygen permeability of SPSEBS is one order lesser than Nafion, thus making it suitable for maintaining anaerobic environment in the anode chamber of the MFC resulting in an increase of CE and power density. The study on the effect of membrane on solution pH using SPSEBS shows that the development of low pH gradient between anode and cathode influences the performance of the MFC.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jpowsour.2012.05.053.

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